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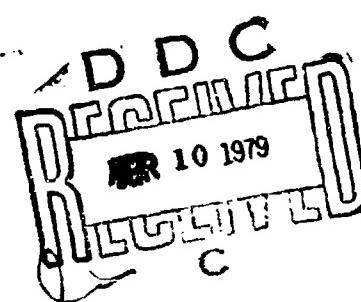
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TECHNICAL REPORT

⑥ THE USE OF PERMEATION TUBES  
AS PRIMARY STANDARDS IN THE  
CALIBRATION OF FLAME PHOTOMETRIC  
DETECTORS AT LOW CONCENTRATIONS.



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## I. INTRODUCTION

The development of sensitive organophosphorus air sampling detection devices has created a need for a simple, accurate and precise method by which known concentration gas mixtures can be generated in the parts per million or the parts per billion range. These gas mixtures are required to calibrate the detection devices. This report describes a simple means by which flame photometric detectors (FPD) can be accurately and reliably calibrated at very low concentrations.

## II. BACKGROUND

There are two principle means by which gas standards are prepared in the laboratory; static and dynamic. Each has certain advantages and disadvantages.

The static method of preparing gas standards involves the addition of known quantities of materials (gases) to a storage container where they are stored until used. This method is simple and accurate at relatively high concentrations. Standards prepared in compressed gas cylinders, glass dilution bottles or plastic bags are prime examples of this method. The disadvantages of the method are contamination, reaction, or absorption of the gas in the container or leakage of the gas from the container.

In the dynamic method, gases are mixed in a flowing system at known flow rates. The major advantage of this system is that it allows flexibility in varying the composition and concentration of the gases. However, it has been difficult to accurately attain the subpart per million concentration range employing this method.

In 1966, O'Keefe and Ortman<sup>1,2</sup> first described the use of permeation tubes in the preparation of primary standards (trace quantities) of volatile atmospheric pollutants. Permeation tubes have all the advantages of the dynamic systems plus simplicity and accuracy. Permeation tubes consist simply of sealed sections of FEP Teflon tubing containing the liquified compound under pressure. For low volatility substances they may be prepared by placing the liquid in Teflon tubing and sealing both ends with metal balls or Teflon plugs.

The filled tubes are placed in a flow system at a carefully controlled temperature and are swept with an air stream whose flow rate is precisely measured. Temperature affects the vapor pressure exponentially; hence, it should be controlled within  $\pm 0.1^{\circ}\text{C}$  or less.<sup>3</sup> Each tube must be "aged"

<sup>1</sup>O'Keefe, A. E., and Ortman, G. C.: Primary Standards for Trace Gas Analysis. *Anal. Chem.* 38, 760 (1966).

<sup>2</sup>Ibid., 39, 1047 (1967).

<sup>3</sup>Scaringelli, F. P., Frey, S. A., and Saltzman, F. E.: Evaluation of Teflon Permeation Tubes for Use with Sulfur Dioxide. *Amer. Ind. Hyg. Ass. J.*, 28, 260 (1967)

for a few days before uniform permeation is achieved.<sup>4</sup> Thereafter, the permeation rate is constant until most of the contained liquid has passed out of the tube. The permeation rate of the tubes are determined gravimetrically by measuring the weight loss of the filled tube each day for several days. For a more detailed discussion of the performance characteristics of these devices, refer to a study by Lucero.<sup>5</sup>

### III. PREPARATION OF PERMEATION TUBES

Permeation tubes were prepared for the simulants trimethyl phosphate (TMP) and dimethyl methylphosphonate (DMMP). These liquids permeate at such a slow rate through regular FEP Teflon that they must be heated to at least 75°C in a permeation tube oven. Although any inert plastic may be used to construct the permeation tube, some plastics are more porous than others. Recently, we found that cross-linked heat shrinkable FEP Teflon allows a satisfactory permeation rate with TMP and DMMP at room temperature. Tubes were constructed from this material by inserting a Teflon plug into one end of a selected length of the expanded tubing, and carefully heating this end (around the plug) shrinking the tube. The tube was then filled with desired liquid (either TMP or DMMP) leaving approximately a 10 percent void. Another Teflon plug was inserted into the other end of the tube, and the tubing end heated to shrink the tube around the second plug. The tube was then heated in an oven to reduce the time necessary to reach a steady-state permeation rate. This was done at 120° to 130°C for 48 hours. This is approximately equivalent to equilibrating at 25°C for 10 days. The tube was then placed in the permeation oven and calibrated gravimetrically.

Permeation tubes were also prepared for phosphine. These tubes are extremely reliable but must be protected from light. A thick walled (0.317 centimeter) Teflon tube was used for physical strength and was capped at one end with a Swagelok cap. The other end was fitted with a stainless steel Nupro check valve. Prior to filling, air was flushed from the tube. Phosphine is condensed under pressure in the tube by cooling in a dry ice-acetone bath.

Care must be exercised when preparing phosphine permeation tubes. The tubing connecting the phosphine pressure bottle (we used lecture bottle size) to the permeation tube must be free of grease, etc. In addition, care must be taken to insure phosphine does not collect or condense on the outside of the tube since this chemical is pyrophoric.

<sup>4</sup>Martin, A. J., Debbrecht, F. J., and Umbreit, G. R.: Devices for Preparing Low-Level Gas Mixtures. Analytical Instrument Development, Inc. West Chester, PA.

<sup>5</sup>Lucero, D. P., Performance Characteristics of Permeation Tubes. Anal. Chem., 43, 1944 (1971).

#### IV. EVALUATION OF PERMEATION TUBES

Many factors regulate the permeation rate obtained from each tube and these must be taken into account when constructing a tube to produce a desired concentration of the calibrating chemical. These include, temperature, length of the permeation tube, thickness of the tubing wall, the type of plastic used in the tubing, and the chemical placed in the permeation tube.

The temperature of the permeation oven may be varied in order to change the permeation rate of a chemical. It was found that as little as a 30°C temperature change in the permeation tube oven temperature produced a significant change in the permeation rate of phosphine. This is shown in Figure 1.

The results plotted in Figure 1 indicates the flexibility that can be obtained in establishing concentrations of phosphine in air simply by varying the temperature. However, if the permeation tube oven has poor temperature control, sizeable errors in calibration will result.

The length of the permeation tube is another parameter which may be used to vary the quantity of a chemical leaving the tube in a given time period. Tubes of various lengths, containing phosphine, were placed in a permeation oven set at 20°C. The results are shown in Figure 2.

As can be seen from these data, the quantity of a chemical permeating the tubes can be varied over a wide range, at a fixed temperature, depending on the length of the permeation tube. Even smaller quantities than achieved with the three permeation tubes used in this study may be obtained if wafer-shaped permeation devices are used.<sup>4</sup> These devices are narrow diameter steel or heavy glass tubes, filled with a specific chemical, and the end covered with a small wafer of Teflon. The wafer is held in place with a heavy compression spring. The effective permeation area can be less than 1.0 square centimeter. Quantities one-thirtieth that of a permeation tube one centimeter long have been reported using wafer permeation tubes.

The thickness of the tubing walls and the composition of the plastic used to make the tubing can also affect the permeation rate. Two tubes of FEP Teflon were filled with TMP. One tube had a wall 0.317 centimeter thick while the other tube wall was 0.159 centimeter thick. A third tube of heat shrinkable cross-linked FEP Teflon containing TMP was prepared. The three tubes were aged and placed in ovens. The first two were maintained at 117°C while the cross-linked FEP was held at 35°C. The results are shown in Table 1.

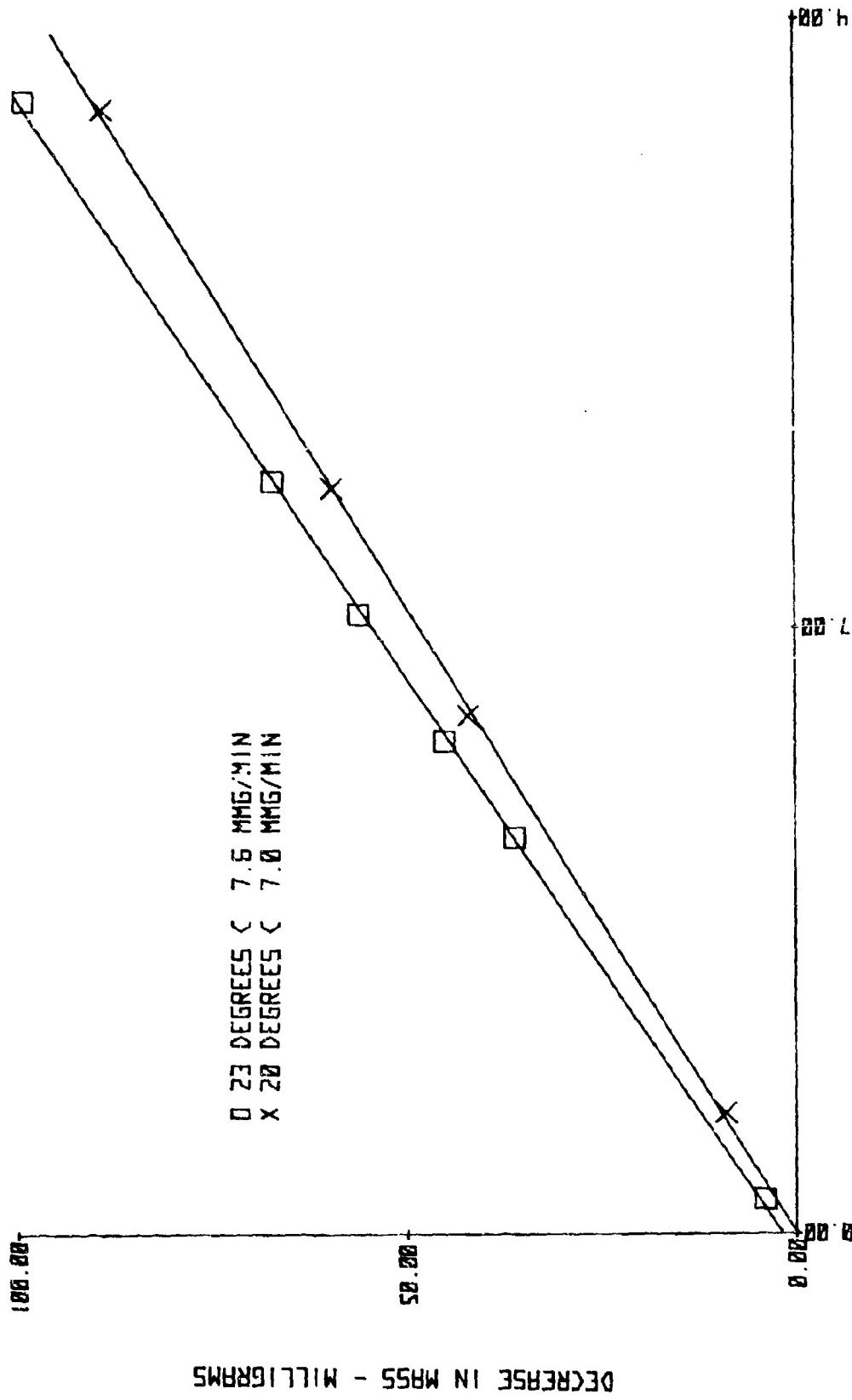


Figure 1. The effect of temperature on the permeation rate of phosphine in a 6.5 cm tube

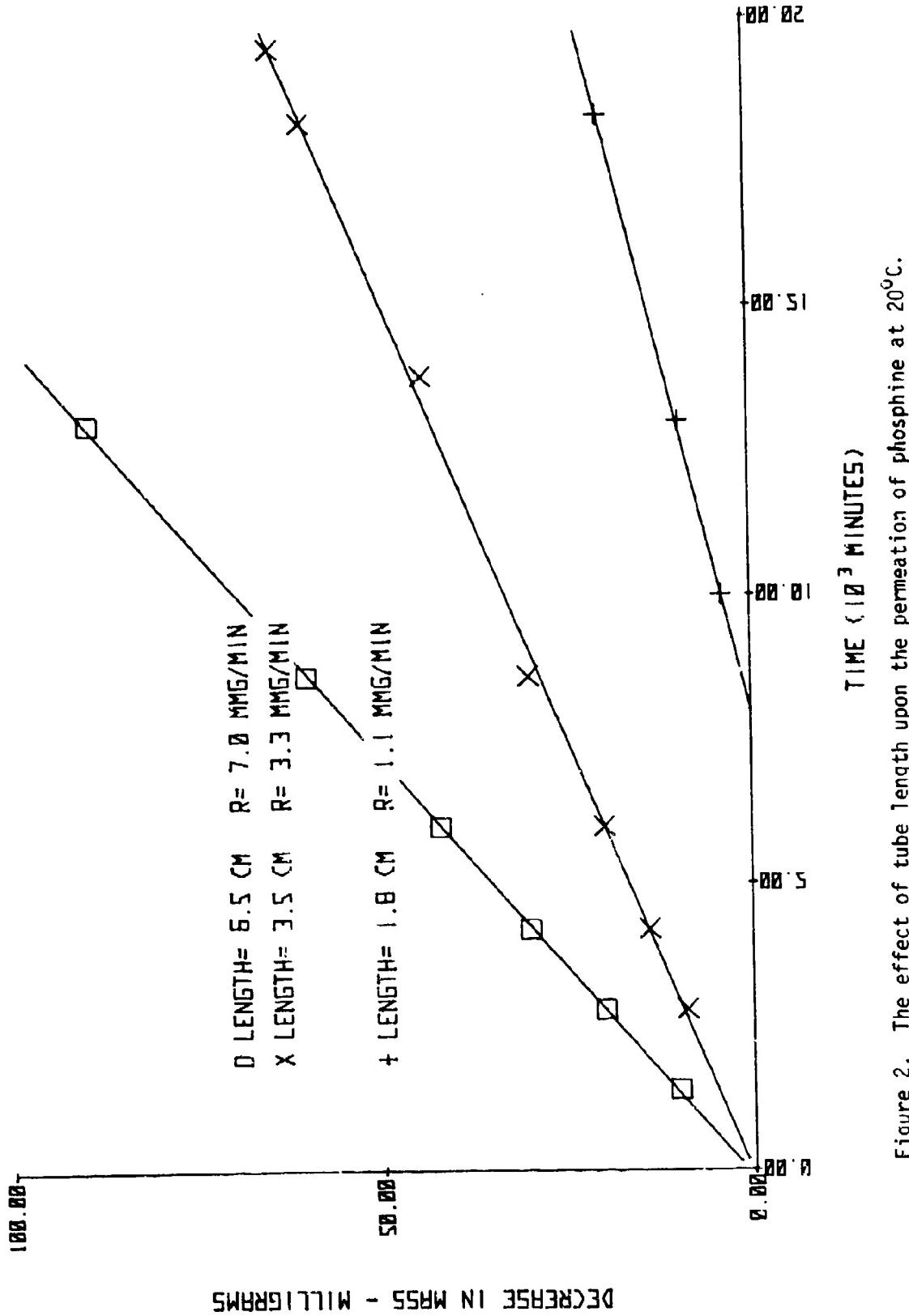


Figure 2. The effect of tube length upon the permeation of phosphine at  $20^\circ\text{C}$ .

Table 1. The effect of wall thickness and type of Teflon used on permeation rates of TMP

Type of Teflon	Wall Thickness (cm)	Temperature of Oven (°C)	Length of Tube (cm)	Permeation Rate of TMP (mmg/minute)
FEP Teflon	0.159	117	4.2	0.70
FEP Teflon	0.317	117	3.6	0.30
Cross-Linked FEP Teflon	--	35	3.0	1.14

Phosphine permeated the FEP Teflon much faster than did TMP or DMMP. The phosphine molecule is much smaller than the other two compounds and if protected from light the tube can be expected to last for several months. In addition, the aging time required to reach a steady-state for phosphine is much shorter. The principle advantage to be gained from using TMP and/or DMMP in calibrating phosphorous detectors is the ease of handling. As mentioned before, phosphine is pyrophoric and is also highly toxic.

A number of portable permeation tube ovens are available commercially. These ovens vary in flexibility depending upon cost. However, even a relatively inexpensive oven will control the temperature of the tube and the air flowing through the oven to 0.1°C or less. The temperatures available usually cover a range of 5° to 50°C above ambient. Variable air flow rates (3 or 4 flow rates) are also included.

#### V. CONCLUSIONS

Permeation tubes can be used as primary standards in the calibration of flame photometric detectors. The tubes are simple to construct, and are reliable and precise in their operation. By carefully selecting the type of plastic used in the construction of the tube, the dimensions of the tubes, and the temperature and air flow rate of the permeation oven, a fairly wide range of concentrations of calibrating chemicals can be obtained.

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